

58. The combination of claim 57 wherein the coupling agent is unreactive except at elevated temperature at which the substrate is printed and cured. ] 112

59. The combination of claim 57 wherein at least some of the microbeads are without the retroreflective elements.

60. The combination of claim 57 wherein the binder chemical and the coupling agent are selected from the group consisting of:

a polyvinylidene chloride copolymer is the binder chemical and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer is the coupling agent,

an acrylic copolymer is the binder chemical and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer is the coupling agent, and

a polyurethane is the binder chemical and blocked 1, 6 hexamethylene diisocyanate trimer is the coupling agent.

61. The combination of claim 57 further comprising one or more components selected from the group consisting of:

pigment, humectant, urea, urea and 2,3 propane diol, buffer, ammonium or sodium phosphates buffer, dispersant, defoamer, thickening agent, cross-linking agent, softening agent, carbon black, UV absorbing material, anti-scuffing agent, a silicone or fluoropolymer, light spill-suppressing agent, anti-static agent, water repellent agent, a silicone, and a fluoropolymer.

62. The combination of claim 57 wherein the volume ratio of the binder to the microbeads is equal to or less than 50%.

63. The combination of claim 57 wherein essentially all of the microbeads are unmetallised and the retroreflective elements include reflective flake particles.

64. The combination of claim 57 wherein the binder forms at least part of a liquid carrier medium for the retroreflective elements or microbeads.

65. The combination of claim 57 wherein the binder chemicals, retroreflective elements and microbeads are comprised of a one-pack retroreflective ink or a two-pack retroreflective ink having the coupling agent as the second pack.

66. The combination of claim 65 wherein the two-pack ink includes a reactive polyisocyanate or an alkoxysilyl alkyl derivative.

67. The combination of claim 57 wherein the microbeads are metallised with an aluminium coating that is superposed on stannous chloride.

68. The combination of claim 67 wherein the microbeads are treated with a compound selected from the group consisting of a silicate, a sodium silicate, a silane, an amino silane, a bis-[gamma-(trimethoxysilyl) propyl] amine and stannous chloride.

69. The combination of claim 67 wherein the metallised microbeads are coated with a silicate or silane that is superposed on the metallised microbeads.

70. A composition that is a one-pack or a two-pack retroreflective ink which is comprised of the combination claimed in claim 57.

71. The composition of claim 70 wherein the retroreflective ink is water-based.

72. The composition of claim 71 that is suitably formulated for screen printing.

73. The composition of claim 70 wherein the ink has a viscosity that is less than or equal to about 40 pascals at room temperature.

74. A composition that is microbeads for use in the production of a retroreflective ink, the microbeads having applied thereto one or more of the group comprising silicate, a silane, an amino silane, bis-[*gamma*-(trimethoxysilyl) propyl] amine and stannous chloride.

75. The composition of claim 74 wherein the microbeads are metallised with a coating of aluminium superposed on the stannous chloride.

76. The composition of claim 75 wherein the silicate is superposed on the metallised aluminium coated beads and the silane is superposed on the silicate.

78. The composition of claim 74 wherein the microbeads have one or more of the following characteristics selected from the group consisting of: a refractive index in the range of about 1.8 to 2.2, a median size of the microbeads in the range of about 10 to 100 microns and the microbeads are composed of titanium glass or barium glass.

79. A composition that is a retroreflective ink which contains microbeads as claimed in claim 74.

80. The composition of claim 78 which includes binder chemicals for attaching the

microbeads to a substrate to which the ink is to be applied.

81. / The composition of claim 80 which includes a coupling agent for coupling the microbeads and for cross-linking the binder chemicals, the coupling agent being unreactive until the printing process is carried out.

82. / A method for making a one-pack retroreflective ink comprising the steps of:

- (a) making microbeads;
- (b) suspending the microbeads in a liquid carrier medium, the liquid carrier medium is comprised of binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied and a coupling agent which couples the microbeads and cross-links the binder chemicals, the coupling agent being unreactive except at elevated temperature at which the printed substrate is cured.

83. / The method of claim 82 wherein step (a) includes applying an aluminium coating to the microbeads.

84. / The method of claim 83 wherein step (a) includes pre-treating the microbeads with stannous chloride prior to application of the aluminium coating.

85. / The method of claim 84 wherein step (a) includes treating the microbeads with a dilute aqueous solution of stannous chloride.

86. / The method of claim 82 wherein step (a) includes hemispherically metallising the microbeads in a vacuum metallising process in which the microbeads are held on a film with

an adhesive coating for transport through the metallising process, the adhesive coating is comprised of styrene-butadiene type adhesive.

87. ✓ The method according to claim 86 wherein step (a) includes passing the film through an aqueous solution of citric acid after metallisation..

88. ✓ The method of claim 86 wherein step (a) includes ultrasonically treating the film to assist in release of the microbeads from the adhesive .

89. ✓ The method of claim 85 wherein step (a) includes treating the microbeads prior to inclusion in the ink with a silicate.

90. ✓ The method of claim 82 wherein step (a) includes treating the microbeads with a silane or an amino silane prior to inclusion in the ink.

91. ✓ The method of claim 89 wherein step (a) includes treating the microbeads with a compound selected from the group consisting of a silane, an amino silane and bis-[gamma-(trimethoxysilyl) propyl] amine after the silicate treatment.

92. ✓ The method of claim 82 wherein step (a) includes adding an amino silanetriol or a blocked polyisocyanate to the liquid carrier medium as coupling agent.

93. ✓ The method of claim 82 wherein step (a) includes preparing the liquid carrier medium from the binder chemicals and the coupling agent before suspending the microbeads in the liquid carrier medium.

94. The method of claim 93 wherein the liquid carrier medium of step (b) includes additives selected from the group consisting of:

pigment, humectant, urea, urea and 2,3 propane diol, buffer, ammonium or sodium phosphate buffer, dispersant, defoamer, thickening agent, cross-linking agent, softening agent, carbon black, UV absorbing material, anti-scuffing agent, silicone, fluoropolymer, light spill-suppressing agent, anti-static agent and water repellant agent.

95. The method of claim 94 wherein step (b) includes adding a thickener to the liquid carrier medium before or after the addition of the binder chemicals and coupling agent.

96. A composition of an ink produced by the method of claim 82.

97. A composition of a substrate coated or printed with a composition of claim 96.

98. The composition of claim 97 wherein the substrate is a screen for displaying projected images or a studio background for chroma-keying applications.

99. The composition of claim 97 wherein the substrate is a flexible tape.

100. The method of providing a substrate having a retroreflective coating, comprising the steps of:

applying to the substrate an ink as claimed in claim 96 wherein the ink is formulated as a one-pack retroreflective ink and the coupling agent is activated after the ink is printed or coated on to the substrate.

101. The method of claim 100 wherein the coupling agent is activated by curing the ink coating at elevated temperature.

102. The method of claim 100 wherein the coupling agent is activated by UV light or other high energy radiation during or after the printing process.

103. A composition that is a retroreflective one-pack ink having a storage life of not less than about 3 months.

104. The composition of claim 103 wherein the retroreflective one-pack ink has a viscosity of between about 10 and 30 pascal after storage of not less than about 3 months.

105. The composition of claim 103 wherein the retroreflective one-pack ink has a laundering durability such that the retroreflectivity is not reduced by more than about 40% when applied to a substrate in the form of a cotton, nylon or polyester fabric and laundered for 5 cycles in accordance with ISO 6330, method 5A.

106. A composition of a fabric having fireproof or fire retardant properties that is printed or coated with a retroreflective ink which is comprised of retroreflective elements in a polymeric matrix, the fabric comprising a structural component that chars before it melts.

107. The composition of claim 106 wherein the fabric is made fireproof or fire retardant by application of a fire retardant agent.

108. The composition of claim 107 wherein the fire retardant agent is applied to a cellulosic, the fire retardant agent is selected from the group consisting of Proban ® and